Noble-Metal Nanotubes (Pt, Pd, Ag) from Lyotropic Mixed-Surfactant Liquid-Crystal Templates

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A. Structural parameters of surfactant molecules

For $C_{12}EO_9$ (i = 1) and Tween 60 (i = 2) molecules, the van der Waals volumes of their hydrophilic head and hydrophobic tail groups, $V_{h,i}^*$ and $V_{t,i}$, were calculated on the basis of the volume increments of atomic groups theoretically obtained by Slonimskii et al. $^{[15]}$ On the assumption that (A1) the hydrophilic head groups have a random conformation to form a spherical block, the effective volume of the spherical head, $V_{h,i}$, and its diameter, $D_{h,i}$, are evaluated by using the following equations:

$$V_{h,i} = V_{h,i}^*/0.681 \text{ and } V_{h,i} = (4\pi D_{h,i}^3/3),$$

where the constant of 0.681 is the packing coefficient fitted to a number of widely differing amorphous and slightly crystalline polymer molecules. $^{[16]}$

The tail lengths, $L_{t,i}$, were calculated by assuming that (A2) the dodecyl and the stearate chains are fully extended with their trans zigzag conformation and that (A3) the $-CO_2-$ group in the latter is chemically hydrophilic but effectively serves as a part of the tail group in the mixed surfactant rodlike micelles.

The molecular volume and length, $V_{m,i}$ and $L_{m,i}$, are given by the equations $V_{m,i} = V_{h,i} + V_{t,i}$ and $L_{m,i} = D_{h,i} + L_{t,i}$, respectively. The results of these calculations are listed in Table S1.
B. Structure models of mixed and single surfactant cylindrical rodlike micelles

For the individual cylindrical rod-like micelle, we can reasonably assume that

(B1) the outer diameter of the cylindrical rod, \( D_r \), is equal to the observed rod-to-rod distance of the hexagonal array,

(B2) the outermost layer of the cylindrical rod is constructed of the spherical heads of \( i=2 \) that are arranged closely parallel to the rod axis and along the circumference on the cylindrical surface of radius \( R_{h,2} - D_{h,2}/2 \), where \( R_{h,2} \) is the distance from the rod axis to the center of the head,

(B3) the tail groups of all the surfactant molecules constituting the cylindrical rod are tilted by the same angle of \( \theta \) with respect to the rod axis so that the terminal methyl groups of the surfactant molecules are lined up in close contact with each other to make a round along the same circumference of radius \( R_{t,i} \),

(B4) the downward four-coordinated holes of the outermost layer are fully occupied by the spherical heads of \( i=1 \) molecules to form the second outermost layer of the rod, leading to the hydrophilic shell with the thickness of \( \delta \).

On the above assumptions we can define a set of structural parameters, including the diameter of hydrophobic core, \( D_c \), and the thickness of hydrophilic shell, \( \delta \), (Table S1, Figure S1) and derive their relations (Table S2). For example, if each \( N \) surfactant molecules make one round
of the cylindrical rod, $N$ is given by the round of the rod ($=2\pi R_{h,i}$) divided by the diameter of the head ($=D_{h,i}$) or $N=2\pi R_{h,i}/D_{h,i}$, where $R_{t,i}$ is the distance from the rod axis to the center of the spherical head. We thus calculated successively the structural parameters listed in Table S1 using the values of $V_{h,i}$, $V_{t,i}$, $V_{m,i}$, $D_{h,i}$, $L_{t,i}$, and $L_{m,i}$ (Table 1), $Dr=6.90$ nm, $D_{Me,i}=0.18$ nm, and $V_{Me,i}=0.023$ nm$^3$, where $D_{Me,i}$ and $V_{Me,i}$ are the diameter and volume of the terminal methyl group, respectively. Some of the data are summarized in Table 2.
Table S1. List of symbols.

- $V_{h,i}$: effective volume of head group of surfactant $i$
- $V_{t,i}$: volume of tail group of surfactant $i$
- $V_{m,i}$: volume of surfactant $i$
- $V_{Me,i}$: volume of terminal methyl group of surfactant $i$
- $D_{h,i}$: effective diameter of head group of surfactant $i$
- $L_{t,i}$: length of tail group of surfactant $i$
- $L_{m,i}$: length of surfactant $i$
- $D_{Me,i}$: diameter of terminal methyl group of surfactant $i$
- $D_r$: diameter of cylindrical rod

- $\theta$: tilt angle of surfactant molecular axis with respect to the rod axis
- $R_{h,i}$: distance from rod axis to the center of head group of surfactant $i$
- $R_{t,i}$: distance from rod axis to the center of terminal methyl group of surfactant $i$
- $N$: number of surfactant molecule per round of rod
- $V$: volume of cylindrical rod-like micelle with the unit length of $D_{h,i}$ ($i=2$)
- $R_{c,i}$: distance from rod axis to the bottom of head group of surfactant $i$
- $D_c$: diameter of hydrophobic core of micelle
- $\delta$: thickness of hydrophilic shell of cylindrical rod-like micelle
- $L_{t,i'}$: distance of the tail part of surfactant $i$ occupying hydrophilic shell
- $V_{t,i'}$: volume of the tail part of surfactant $i$ occupying hydrophilic shell
- $V_s$: volume of hydrophilic shell with the unit length of $D_{h,i}$ ($i=2$)
- $V_s^m$: volume of molecular skeleton occupying hydrophilic shell with the unit length
- $V_s^g$: volume available for guest species within hydrophilic shell with the unit length
- $V_j$: volume of guest species $j$
- $x_j$: mole fraction of guest species $j$
- $P_r$: volume fraction of surfactant molecules occupying the micellar volume
- $P_g$: volume fraction of all guest species $j$ occupying $V_s^g$
Table S2. List of relations.

\[ R_{h,2} = \frac{D_r - D_{h,2}}{2} \]

\[ R_{t,i} = R_{h,2} \sqrt{\frac{V_{Me,2}}{V_{h,2}}} \]

\[ \theta = \sin^{-1}\left(\frac{R_{h,2} - R_{t,2}}{L_{m,2} - (D_{h,2} + D_{Me,2})/2}\right) \]

\[ N = \frac{2\pi R_{h,2}}{D_{h,2}} \]

\[ V = \pi \left(\frac{D_r}{2}\right)^2 \times D_{h,2} \]

\[ P_r = \frac{N(V_{m,1} + V_{m,2})}{V} \]

\[ R_{c,i} = (L_{m,i} - \frac{D_{h,i} + D_{Me,i}}{2}) \sin \theta - \frac{D_{h,i}}{2} + R_{t,i} \]

\[ D_c = 2R_{c,1} \]

\[ \delta = \frac{D_r}{2} - R_{c,1} \]

\[ L_{t,2}' = \frac{(R_{c,2} - R_{c,1} + D_{h,2}/2)}{\sin \theta} - \frac{D_{h,2}}{2} \]

\[ L_{t,1}' = \frac{D_{h,1}/2}{\sin \theta} - \frac{D_{h,1}}{2} \]

\[ V_{t,i}' = V_{t,i} \frac{L_{t,i}'}{L_{t,i}} \]

\[ V_s = V - \pi \frac{D_c^2}{4} \times D_{h,2} \]

\[ V_s^m = N(V_{h,1} + V_{h,2}) + N(V_{t,1}' + V_{t,2}') \]

\[ V_s^g = V_s - V_s^m \]

\[ P_s = \frac{N \Sigma V_j X_j}{V_s^g} \]
Figure S1. Schematic representation of several structural parameters.